



Solar photo-Fenton treatment of pesticides in water: Effect of iron concentration on degradation and assessment of ecotoxicity and biodegradability

A. Zapata^a, T. Velegraki^b, J.A. Sánchez-Pérez^c, D. Mantzavinos^b, M.I. Maldonado^a, S. Malato^{a,*}

^a Plataforma Solar de Almería (CIEMAT), Carretera Senés, Km 4, 04200 Tabernas (Almería), Spain

^b Department of Environmental Engineering, Technical University of Crete, Polytechniopolis, GR-73100 Chania, Greece

^c Department of Chemical Engineering, University of Almería, Crta de Sacramento s/n, 04120 Almería, Spain

ARTICLE INFO

Article history:

Received 2 July 2008

Received in revised form 22 October 2008

Accepted 25 October 2008

Available online 11 November 2008

Keywords:

Biodegradability

Detoxification

Pesticides treatment

Photocatalysis

Solar photo-Fenton

ABSTRACT

A combined solar photo-Fenton and biological treatment is proposed for the decontamination of a mixture of five commercial pesticides commonly used in intensive agriculture Vydate (10% Oxamyl), Metomur (20% Methomyl), Couraze (20% Imidacloprid), Ditimur-40 (40% Dimethoate) and Scala (40% Pyrimethanil). Photo-Fenton experiments were conducted in a solar pilot reactor consisting of four compound parabolic collectors in which the pesticide mixture was treated at an original dissolved organic carbon (DOC) concentration of 200 mg/L in the presence of Fe^{2+} or Fe^{3+} concentration of 5, 20 and 55 mg/L. Ferrous ions were marginally more active than ferric in terms of active ingredient degradation, which followed zero order kinetics, more so in the early reaction stages. Photo-Fenton was also far more effective (by at least two orders of magnitude) than the respective dark reaction under identical experimental conditions.

Irradiation for 50–100 min (normalized at 30 W/m² light intensity) at 20 mg/L Fe^{2+} was able to completely eliminate the active ingredients, and reduce DOC by about 15–50% and COD by 40–70%, respectively. At these conditions, ecotoxicity to the marine bacteria *V. fischeri* was substantially lessened, while aerobic biodegradability in tests with activated sludge was enhanced.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Agrochemical wastewater from widespread intensive greenhouse agriculture in the Mediterranean Region is polluting water with pesticides. New generation pesticides, such as those employed in this study, are highly soluble in water, involving significant risk to aquatic ecosystems and water resources. Their low-sorption affinity to soils rapidly leads to extensive groundwater and surface water contamination. These compounds, often toxic, chemically stable and difficult to mineralize, have been proven recalcitrant to biological treatment. Due to their persistence and bio-accumulation, and consequent long-term toxicity, they have been designated as priority substances in EU legislation [1].

Advanced oxidation processes (AOPs) are effective treatment methods for these pollutants, and may be considered promising alternatives to conventional technologies, such as activated carbon adsorption and incineration [2]. AOPs are characterized by the production of hydroxyl radicals ($\cdot\text{OH}$), which are powerful, unselective oxidants (2.8 V vs. standard hydrogen electrode).

Their advantage is that they are able to oxidize and mineralize almost any organic molecule, yielding CO_2 and inorganic anions. However, their main drawback is their relatively high operating costs compared to biological treatment [3]. As a means of reducing treatment cost, scientific interest has focused on photocatalytic processes driven by solar irradiation [4,5]. Another way to reduce costs is to follow an AOP that transforms toxic or recalcitrant compounds into biodegradable intermediates (not to complete the mineralization, which could reduce AOPs treatment time) with a biotreatment [6–8].

This paper deals with the use of a solar-driven Fenton process to treat a mixture of commercial pesticides. The main purpose is to determine optimal photo-Fenton conditions (i.e., type and concentration of iron ions, treatment time) for making wastewater biocompatible and suitable for subsequent biological treatment. Wastewater containing commercial pesticides was tested to optimize the treatment not only for the active ingredients, but also for other compounds in the commercial formulations. The main goal was to optimize the photo-Fenton treatment selecting the most suitable Fe species (Fe^{2+} or Fe^{3+}), the best concentration of Fe for the solar photoreactors, and the minimum treatment time. Furthermore, Fenton and photo-Fenton were compared to find the main differences between the two processes.

* Corresponding author. Tel.: +34 950 387940; fax: +34 950 365015.

E-mail address: sixto.malato@psa.es (S. Malato).

2. Experimental

2.1. Chemicals

Commercial formulations of Vydate[®] (10%, w/v oxamyl, C₇H₁₃N₃O₃S), Metomur[®], (20%, w/v methomyl, C₅H₁₀N₂O₂S), Couraze[®] (20%, w/v imidacloprid, C₁₆H₂₂ClN₃O), Ditimur-40[®] (40%, w/v dimethoate, C₅H₁₂NO₃PS₂) and Scala[®] (40%, w/v pyrimethanil, C₁₂H₁₃N₃) were used as received. Scheme 1 shows the chemical structures of the pesticides. Water solubility of these compounds is 0.61 g/L, 20 °C (Imidacloprid); 280 g/L, 25 °C (Oxamyl); 23.8 g/L, 25 °C (Dimethoate); 57.9 g/L, 25 °C (Methomyl) and 0.121 g/L, 25 °C (Pyrimethanil). Analytical standards (>98%) for chromatographic analyses were purchased from Sigma-Aldrich.

Distilled water used in the pilot plant was supplied by the Plataforma Solar de Almería (PSA) distillation plant (conductivity < 10 µS/cm, Cl[−] = 0.2–0.3 mg/L, NO₃[−] < 0.2 mg/L, organic carbon < 0.5 mg/L). The experiments were performed using iron sulfate heptahydrate (FeSO₄·7H₂O), iron chloride hexahydrate (FeCl₃·6H₂O), reagent-grade hydrogen peroxide (30%, w/v) and sulfuric acid for pH adjustment (around 2.7–2.9), all purchased from Panreac. The phototreated solutions were neutralized by NaOH (reagent-grade, Panreac) for toxicity and biodegradability analyses.

2.2. Analytical determinations

High-performance liquid chromatography HPLC (Agilent Technologies, series 1100) was used to monitor the pesticide concentration during degradation with a UV-DAD detector and a C-18 column (LUNA 5 µm, 3 mm × 150 mm from Phenomenex) as the stationary phase. The mobile phase consisted of a mixture of 15% acetonitrile, HPLC grade and 85% ultrapure water (Millipore Co.). Detection was done at three different wavelengths depending on the pesticide found in the mixture: 210 nm (Dimethoate and Pyrimethanil), 234 nm (Methomyl and Oxamyl) and 270 nm (Imidacloprid). Mineralization was followed by measuring the dissolved organic carbon (DOC) by direct injection of filtered

samples (PTFE 0.22 µm, Millipore Millex[®] GN) into a Shimadzu-5050A TOC analyzer with an NDIR detector and calibrated with standard solutions of potassium phthalate. Chemical oxygen demand (COD) was measured with Merck[®] Spectroquant kits (ref: 1.14541.0001). Total iron concentration was monitored by colorimetric determination with 1,10-phenanthroline, according to ISO 6332, using a Unicam-2 spectrophotometer. Hydrogen peroxide was analyzed by a fast, simple spectrophotometric method using ammonium metavanadate, which allows the H₂O₂ concentration to be determined immediately based on a red-orange peroxovanadium cation formed during the reaction of H₂O₂ with metavanadate, maximum absorption of which is at 450 nm. The peroxide concentrations are calculated from absorption measurements by a ratio found by Nogueira et al. [9].

2.3. Toxicity and biodegradability assays

A commercial assay marketed as Biofix[®]Lumi-10 was employed to evaluate the toxicity of commercial pesticide solutions partially oxidized by photo-Fenton at different stages of the treatment using a freeze-dried specially-selected strain of the marine bacterium *Vibrio fischeri* (NRRL number B-11177). Toxicity was evaluated in undiluted and 1:10 diluted samples. The drop in light emission of the bacteria after contact periods of 5, 15 and 30 min was measured and compared with a toxicant-free control (2% NaCl solution). Temperature was kept at 15 °C by a thermoblock and sample salinity was adjusted to 2%. Hydrogen peroxide present in the samples was removed prior to toxicity analysis using catalase (2500 U/mg bovine liver; 100 mg/L) acquired from Fluka Chemie AG (Buchs, Switzerland) after adjusting the sample pH to between 6 and 8. The biodegradability of the pesticide mixture was evaluated by the Zahn–Wellens (Z-W) test (Directive 88/303/EEC). Activated sludge from the Aqualia wastewater treatment plant in Almería (0.2–1.0 g/L dry matter), mineral nutrients (2.5 mL/L mineral solution), and 0.24 L of each sample from photo-Fenton experiments at different treatment stages as the sole carbon source, were mixed in a 0.25-L glass vessel (covered with aluminum foil to keep the mixture under diffuse illumination) and kept under constant agitation and aeration. The test lasted 28 days at 20–25 °C. Every two or three days, aliquots were taken, filtered and measured in the TOC analyzer. The ratio of DOC eliminated after each interval to initial DOC is expressed as the percentage of biodegradability. Once the biodegradation percentage reaches 70%, the test sample is considered biodegradable [10].

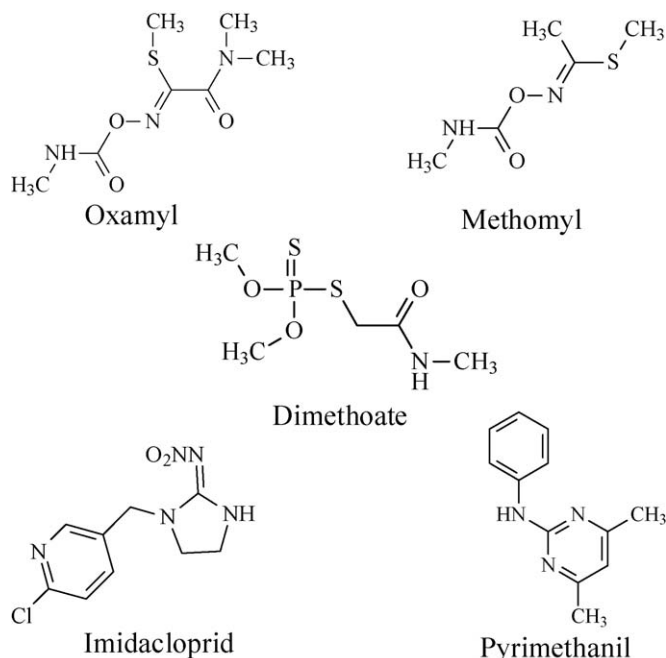
2.4. Experimental set-up

2.4.1. Solar reactors

Photo-Fenton experiments were carried out under sunlight in a pilot plant specially developed for photo-Fenton applications, installed at the Plataforma Solar de Almería (PSA). A diagram of this system has recently been published elsewhere [11]. It consists of four compound parabolic collectors (CPCs), a reservoir tank, a recirculation pump and connecting tubing. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37° (the same as the CPCs). With Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible [12].

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_T}; \quad \Delta t_n = t_n - t_{n-1} \quad (1)$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n , and t_{30W} is



Scheme 1. Pesticide chemical structures.

a “normalized illumination time”. In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon). V_T is the total volume of the water loaded in the pilot plant (75 L), V_i is the total irradiated volume (44.6 L).

All photo-Fenton experiments were carried out at an original DOC of 200 mg/L (40 mg/L of each commercial pesticide) in a distilled water matrix, at a pH adjusted to 2.7–2.9 (H_2SO_4 2N) and hydrogen peroxide concentration kept between 100 and 500 mg/L throughout the process. The temperature inside the reactor was kept at 35°C using a temperature control system. The mixture of pesticides was added directly into the pilot plant and homogenized by turbulent recirculation for half an hour at 35°C . With the collectors covered, the pH was adjusted and iron salt was added. Then 400 mg/L of hydrogen peroxide were added and the collectors were uncovered, which is when photo-Fenton began. Hydrogen peroxide was measured frequently and consumed reagent was continuously replaced so as to maintain excess H_2O_2 .

Fenton experiments were performed in 3-L vessels with continuous agitation. The pH was set at 2.8, the iron concentration was 20 mg/L and the initial H_2O_2 was 300 mg/L. Two initial DOC concentrations were tested with both iron species (Fe^{2+} and Fe^{3+}): 50 and 100 mg/L (10 and 20 mg/L of each commercial pesticide, respectively).

3. Results and discussion

3.1. Photo-Fenton studies

Several photoassisted blank experiments, at the conditions as the photocatalytic assays, were performed to guarantee that the obtained results were consistent and not due to other effects. In the first study, the mixture was irradiated in the photoreactor in mere presence of H_2O_2 (with a concentration maintained between 100 and 300 mg/L). After $t_{30W} = 350$ min and 2 mM of H_2O_2 consumed, all the active ingredients suffered some partial degradation (between 35 and 80%). However, the DOC remained almost stable during all the process, with a final reduction of only 4%. In the second experiment, the degradation process was evaluated only in presence of iron (20 mg/L). In this case, after $t_{30W} = 300$ min, the active ingredients reduction was much lower (between 3 and 17%), and no mineralization was attained. Comparing these results with the photo-Fenton degradation of the mixture (Fig. 1 and Table 1), it can be disregarded any substantial photosensitization of chemical matrix.

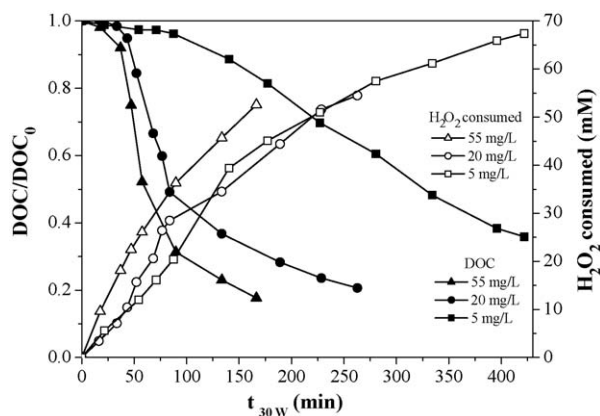


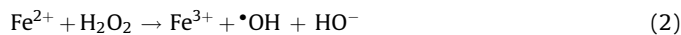
Fig. 1. Mineralization of the pesticide mixture ($\text{DOC}_0 = 200 \text{ mg/L}$) at different Fe^{2+} concentrations with H_2O_2 consumed during the photo-Fenton experiments.

Table 1

Hydrogen peroxide consumption and normalized illumination time required for photo-Fenton degradation of all active ingredients of the commercial pesticide mixture ($\text{DOC}_0 = 200 \text{ mg/L}$) employing different iron species and concentrations.

Iron concentration (mg/L)	Complete degradation of active ingredients		75% mineralization	
	t_{30W} (min)	H_2O_2 (mM)	t_{30W} (min)	H_2O_2 (mM)
Fe^{2+}	5	175	460	75
	20	50	220	50
	55	35	125	48
Fe^{3+}	5	200	500	78
	20	55	220	54
	55	36	155	50

Photo-Fenton degradation of a mixture of five commercial pesticides was evaluated employing two iron species (Fe^{2+} and Fe^{3+}) at three iron concentrations (5, 20 and 55 mg/L), chosen based on previous PSA studies which showed that the optimum range of iron concentration for solar photocatalytic experiments is 0.2–0.5 mM [13]. The compounds were dissolved in distilled water until each active ingredient reached an initial DOC concentration of 40 mg/L, i.e., a mixture with an initial DOC of 200 mg/L. Therefore, the amounts of these active ingredients in the mixture were 84 mg/L of oxamyl, 22 mg/L of methomyl, 20 mg/L of imidacloprid, 32 mg/L of dimethoate, and 54 mg/L of pyrimethanil. Fig. 1 shows mineralization of the pesticide mixture at the three Fe^{2+} concentrations and the corresponding hydrogen peroxide requirements during the processes. The results were very similar to those with Fe^{3+} , especially at low iron concentrations. Table 1 compares hydrogen peroxide consumption and illumination times with the two iron species at three concentrations during the photo-Fenton experiments. No significant difference in DOC was observed between Fe species, although this was not the case for degradation of each individual pesticide, as discussed later (see Table 2). Fe^{2+} salt is rapidly converted to Fe^{3+} if there is excess H_2O_2 (during the first seconds after adding H_2O_2), but the $\cdot\text{OH}$ produced by Fenton reaction (Eq. (2)) are not enough for significant oxidation of organics. When Fe^{3+} salt is used, it is reduced to Fe^{2+} , mainly by solar irradiation and by H_2O_2 (Eqs. (3) and (4)). Irradiation with light up to 580 nm leads to photoreduction of dissolved ferric iron to ferrous iron [14]. The primary step is a ligand-to-metal charge-transfer reaction. Later intermediate complexes dissociate as shown in Reaction (5) [15]. The ligand can be any Lewis base able to form a complex with ferric iron (OH^- , H_2O , HO_2^- , Cl^- , R-COO^- , R-OH , R-NH_2 , etc.). Depending on the reacting ligand, the product may be a hydroxyl radical such as in Eqs. (6) and (7) or another radical derived from the ligand.



Ferric iron complexes absorb light differently depending on the ligand, and Reaction (5) takes place at different wavelengths and

Table 2Zero order kinetic constants (mg/L min), linear regression coefficients (R^2) and standard deviations (SD) for each pesticide in the mixture treated by photo-Fenton.

Compound	Fe ²⁺ (mg/L)			Fe ³⁺ (mg/L)		
	5	20	55	5	20	55
Oxamyl	0.47 (R^2 : 0.99) (SD: 3.18)	1.48 (R^2 : 0.99) (SD: 2.94)	3.62 (R^2 : 0.9) (SD: 3.41)	0.29 (R^2 : 0.91) (SD: 2.87)	1.34 (R^2 : 0.98) (SD: 3.00)	2.50 (R^2 : 0.96) (SD: 3.22)
Methomyl	0.11 (R^2 : 0.98) (SD: 0.87)	0.40 (R^2 : 0.97) (SD: 1.34)	0.55 (R^2 : 0.93) (SD: 2.77)	0.10 (R^2 : 0.91) (SD: 1.14)	0.36 (R^2 : 0.99) (SD: 0.97)	0.47 (R^2 : 0.97) (SD: 1.73)
Imidacloprid	0.11 (R^2 : 0.99) (SD: 0.27)	0.44 (R^2 : 0.99) (SD: 0.85)	1.08 (R^2 : 0.9) (SD: 3.42)	0.10 (R^2 : 0.91) (SD: 0.77)	0.41 (R^2 : 0.99) (SD: 0.92)	0.69 (R^2 : 0.99) (SD: 1.00)
Pyrimethanil	0.24 (R^2 : 0.99) (SD: 0.91)	0.89 (R^2 : 0.96) (SD: 2.76)	0.99 (R^2 : 0.9) (SD: 3.25)	0.24 (R^2 : 0.92) (SD: 1.48)	0.75 (R^2 : 0.98) (SD: 3.21)	1.14 (R^2 : 0.99) (SD: 0.96)
Dimethoate	0.32 (R^2 : 0.99) (SD: 2.42)	0.99 (R^2 : 0.9) (SD: 2.31)	1.69 (R^2 : 0.97) (SD: 3.00)	0.39 (R^2 : 0.97) (SD: 2.58)	1.16 (R^2 : 0.99) (SD: 3.15)	1.56 (R^2 : 0.96) (SD: 3.22)

with different quantum yields. pH plays a crucial role in photo-Fenton reaction efficiency, because it strongly influences which complexes are formed. Thus, pH 2.8 has frequently been postulated as an optimum pH for photo-Fenton treatment, because at this pH there is no precipitation yet and the predominant iron species in the solution is $[\text{Fe}(\text{OH})]^{2+}$, the most photoactive ferric iron–water complex [16].

As the system behaves independently of the initial oxidation state of iron, ferrous iron cannot usually be distinguished from ferric iron by the reaction mechanism. However, in practice, differences in degradation rates may be observed. The presence of Fe^{2+} promotes an initial rapid degradation phase [17]. The extent of this phase depends on the Fe/contaminant molar ratio. On the contrary, when Fe^{3+} is the initial iron source, the oxidation rate is slower than observed with Fe^{2+} , probably due to the fact that as Fe^{3+} is reduced to Fe^{2+} , the free radicals are generated more slowly [18].

It is worth mentioning that with 5 mg/L of iron, treatment is noticeably less efficient (slower pesticide degradation, longer time required for any substantial mineralization and more hydrogen peroxide consumed). This is because when the iron concentration is very low, the catalyst concentration is the photo-Fenton limiter, and H_2O_2 is consumed by less desirable reactions, such as Reaction (8).



There were no significant differences in the parameters mentioned above between the other two iron concentrations (20 and 55 mg/L), although, as expected, results were slightly better with 55 mg/L. This can be explained because, due to the photoreactor design, iron concentration is enough to absorb all the solar irradiation in both cases. Therefore, Reactions (6) and (7) are maximized permitting quick regeneration of the ferrous ions. Under these conditions, the amount of absorbed photons is quite similar at 20 and 55 mg/L of Fe in a solar photoreactor with a 5-cm light pathlength [19].

It should be noticed that the higher the concentration of iron, the fewer photons reach the axis of the photoreactor. However, it may also be said that as iron concentration increases, less hydrogen peroxide is needed for the same degradation. This is because in the presence of higher iron concentrations, the process is accelerated by two added benefits. Firstly, the photocatalytic regeneration of ferrous iron from ferric iron is faster and there are always ferrous ions available to consume H_2O_2 and produce OH^\bullet

radicals. H_2O_2 is also more efficient, as it is mainly consumed in “useful” reactions. When the process is too slow, part of the H_2O_2 is decomposed into molecular oxygen and water but does not participate in the oxidation of the polluting molecules. Eqs. (9)–(11) show some simultaneous reactions occurring in the matrix when the hydrogen peroxide concentration in the solution is too high [20,21].

These reactions reduce overall photo-Fenton effectiveness, as hydrogen peroxide consumption and hydroxyl radical generation are unrelated to organic molecule degradation.



Degradation of the active ingredients contained in the commercial pesticide mixture (oxamyl, methomyl, imidacloprid, dimethoate and pyrimethanil) was monitored during the experiments by HPLC analysis. All the results could be adjusted to zero order kinetics, which means that the degradation rate of each pesticide was not dependent on its concentration, but only on the concentration of hydroxyl radicals, and consequently on iron concentration, since there was excess as H_2O_2 . Hydrogen peroxide concentration was kept between 100 and 500 mg/L, which means that the kinetic constants should increase with iron concentration. Table 2 shows the zero order kinetic constants for each pesticide with regard to photo-Fenton degradation of the commercial pesticide mixture employing both iron species at the three tested concentrations, and an initial DOC of 200 mg/L. As expected, the kinetic constants increase with iron concentration, and more so with Fe^{2+} than with Fe^{3+} due to the initial fast degradation phase explained above. This effect becomes more noticeable as the iron concentration rises (higher Fe/contaminant molar ratio). It might therefore be concluded that when the main purpose is to substantially reduce the organic content of wastewater, it is irrelevant which species of iron is used as long as its concentration is not too high (mM range). The same is true when the reaction time is expected to be longer than a few minutes.

Fig. 2 compares the photo-Fenton degradation of three of the five pesticides (oxamyl, methomyl, pyrimethanil) employing 55 mg/L of Fe^{2+} and Fe^{3+} . Results with the other two pesticides were similar. Two distinctive kinetic regimes are observed in photo-Fenton runs employing Fe^{2+} as the iron source. There is a fast

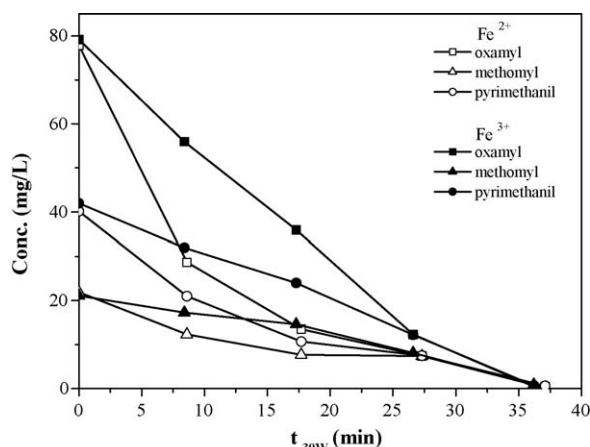


Fig. 2. Photo-Fenton degradation of three pesticides at 55 mg/L of Fe^{2+} and 200 mg/L of initial DOC of the commercial pesticide mixture.

initial phase during the first minutes of the process (sharp slope), followed by a slower phase featuring mild oxidation until complete degradation. Profuse generation of free radicals by oxidation of Fe^{2+} to Fe^{3+} (Reaction (2)) at the beginning could account for this oxidation, which is followed by regeneration of Fe^{2+} that is governed by a reaction promoted by solar irradiation. The same effect was observed at all three tested iron concentrations but was more pronounced at the two higher Fe concentrations.

Of the two iron species, Fe^{2+} was slightly more efficient and 20 mg/L was only slightly slower than with 55 mg/L, permitting adequate evolution of the process without adding as much iron and counter ion (SO_4^{2-}). Based on all these results, 20 mg/L of Fe^{2+} was selected for all the following studies.

3.2. Fenton studies

Fenton degradation of the mixture of commercial pesticides was also evaluated at an iron concentration of 20 mg/L, employing two iron species (Fe^{2+} and Fe^{3+}) at two different original DOC (50 and 100 mg/L). DOC was not 200 mg/L in this study so that substantial degradation could be accomplished in a reasonable length of time. A photo-Fenton experiment with 20 mg/L of Fe^{2+} and 100 mg/L of initial DOC was also carried out for comparison with the effectiveness of Fenton-only under the same operating

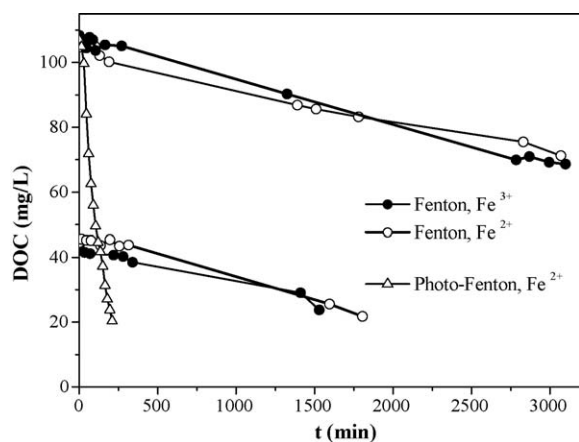


Fig. 3. Comparison of Fenton (Fe^{2+} and Fe^{3+}) at different initial DOC (50 and 100 mg/L) and photo-Fenton (Fe^{2+}) degradation at DOC = 100 mg/L of the commercial pesticide mixture employing 20 mg/L of Fe. Note that t refers to reaction time in both cases.

Table 3

Comparison of Fenton and photo-Fenton (20 mg/L of Fe^{2+}) degradation of the commercial pesticide mixture at an initial DOC of 100 mg/L.

	Fenton	Photo-Fenton
Reaction time for elimination of active ingredients (min)	820	45
H_2O_2 consumed for total elimination of active ingredients (mM)	5.5	6
H_2O_2 consumed for 20% mineralization (mM)	6.7	10
H_2O_2 consumed for 35% mineralization (mM)	10	15

conditions. Fig. 3 compares mineralization of the pesticide mixture by Fenton and by photo-Fenton with both iron species. For easier comparison, the independent variable in photo-Fenton is also expressed as reaction time, instead of normalized illumination time (t_{30W}), as in the previous experiments. The mean solar UV irradiation in the photo-Fenton reaction was 38 W/m².

As in the photo-Fenton experiments, there were no significant differences in dark Fenton degradation of the mixture when using Fe^{2+} or Fe^{3+} . Fe^{2+} was converted in Fe^{3+} by Reaction (2) but only a few $\cdot\text{OH}$ are produced due to the low iron concentration (20 mg/L). Only Reactions (3) and (4) could reduce Fe^{3+} to Fe^{2+} , and therefore both have the same behavior (concerning mineralization) beyond the initial stage. Photo-Fenton was much more effective (more mineralization, shorter treatment times) than Fenton for the degradation of the mixture of selected commercial pesticides. Table 3 shows a comparison of Fenton and photo-Fenton degradation of the pesticide mixture using different process parameters, with an initial DOC of 100 and 20 mg/L of Fe^{2+} . It may be observed that Fenton alone only mineralized 35% in 3000 min, while photo-Fenton mineralized 80% after 240 min of reaction time, or a t_{30W} of 168 min. On the other hand, hydrogen peroxide consumed was similar for the total elimination of active ingredients in both cases.

Due to these results, Fenton was not considered an attractive option, because of the relatively long treatment time needed to achieve complete degradation of the active ingredients and/or substantial mineralization, and therefore, it was discarded as a pretreatment for combined chemical and biological studies. It is clear that with the use of a higher Fe concentration, Fenton would have yielded better results, but as it is intended to determine the biocompatibility of the commercial pesticide mixture at different stages of the process, the Fe concentration should be minimal. In view of these results, and taking into account solar treatment plant operation, however, Fenton might still be advantageous for the overall efficiency of the treatment. Table 3 shows that less H_2O_2 was consumed in the dark Fenton treatment than in the photo-Fenton treatment for the same mineralization. This means that when a solar photo-Fenton plant is operated, dark periods (night, in a day cycle) could improve the treatment efficiency in two ways, by slowly mineralizing the contaminants at a lower H_2O_2 consumption rate. One constraint is that H_2O_2 concentration during the dark should be low enough to avoid parallel reactions in the matrix which occur with high hydrogen peroxide concentrations (see Reactions (9)–(11)), that could reduce the overall effectiveness and increase the consumption of hydrogen peroxide.

3.3. Toxicity and biodegradability analyses

Toxicity and biodegradability of samples were analyzed at different stages of the photo-Fenton degradation of the pesticide mixture. The aim of these assays was to evaluate likely toxicity reduction and/or biodegradability enhancement following photo-Fenton pretreatment at optimal conditions, i.e., at 20 mg/L of Fe^{2+} .

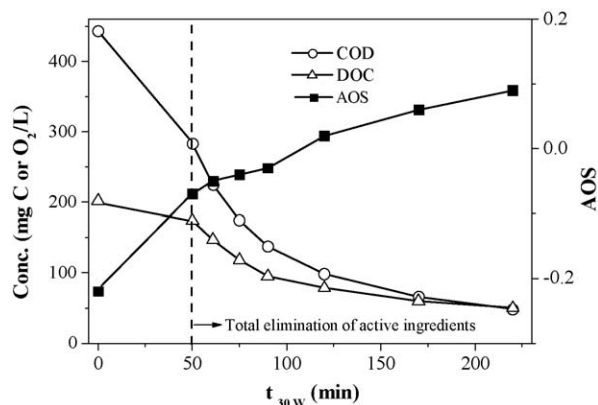


Fig. 4. DOC, COD and AOS evolution during the photo-Fenton degradation of the pesticide mixture at 200 mg/L of initial DOC and 20 mg/L of Fe^{2+} .

In addition to DOC, COD was also measured during photo-Fenton treatment to evaluate the average oxidation state (AOS) of the solution according to Eq. (12) [22]

$$\text{AOS} = \frac{4 \times (\text{DOC} - \text{COD})}{\text{DOC}} \quad (12)$$

where DOC and COD are expressed in molar concentrations. AOS is between +4 for CO_2 , the most oxidized state of C, and −4 for CH_4 , the most reduced state of C. AOS is a valuable parameter that can be used to estimate oxidation in a complex solution consisting of the initial substances and their oxidation by-products. It can also provide indirect information on its biodegradability, as it indicates variations in the composition of the effluent that could result in changes in biodegradability/toxicity of the solution [23]. Fig. 4 shows the progress of COD, DOC and AOS during pesticide mixture degradation by photo-Fenton. AOS increased gradually throughout the experiment. These results suggest that more oxidized organic intermediates were formed during the photo-Fenton process, changing the average chemical nature of the mixture. Formation of more oxidized intermediates is an indirect indication of the ability of the treatment to improve biodegradability. Taking these changes in AOS into account, toxicity and biodegradability studies were performed until 75% mineralization.

Fig. 5 shows toxicity results as a percentage of bacteria inhibition when exposed to samples for 30 min. A 1:10 dilution was also prepared prior to toxicity analysis. Both toxicity curves showed approximately the same tendency. In the 1:10 diluted sample, inhibition decreased from 80% for the non-treated pesticide mixture

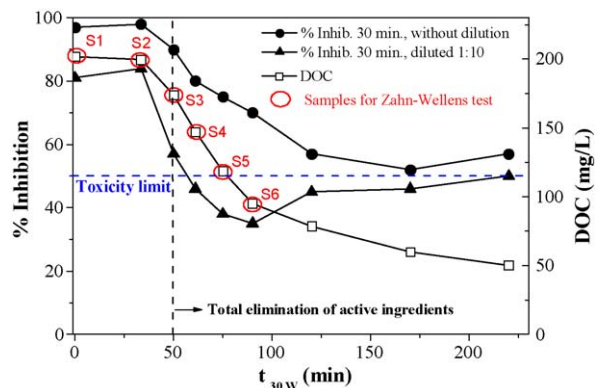


Fig. 5. Percentage of *Vibrio fischeri* inhibition after 30 min exposure to samples partially treated by photo-Fenton at 20 mg/L of Fe^{2+} .

to 50% after treatment with photo-Fenton (final DOC of 50 mg/L), but in between there were stages when toxicity was lower. Interestingly, toxicity reduction was more pronounced in those samples where complete elimination of the active ingredients was achieved. ($t_{30w} = 50$ min, DOC of 175 mg/L). With longer photo-Fenton treatment, toxicity increased slightly, presumably due to the formation of end products to which *V. fischeri* is relatively sensitive. The most important result of the toxicity tests was that it changed continuously during the treatment, and therefore, toxicity evaluation is not a suitable way to determine the moment when biodegradability is most enhanced. However, toxicity results used together with AOS results, are indicating that biodegradability should change dramatically during the process. These assays must therefore be complemented with biodegradability studies.

The Z-W test was performed on six samples (as shown in Fig. 5) taken at different stages of the photo-Fenton process to check their aerobic biodegradability. Sample S1 is the original pesticide mixture, while S2 has been subjected to mild photo-Fenton treatment, and both of them contain active ingredients. Sample S3 contains only traces of these compounds and the rest (Samples S4–S6) are free of pesticides. The concentrations of the five substances in Samples 1 and 2 were also monitored during the Z-W test. Three of them remained constant throughout the assay (methomyl, imidacloprid and dimethoate). However, the oxamyl and pyrimethanil concentrations appeared to decrease throughout the test. Oxamyl behavior can be explained by hydrolysis at neutral pH forming $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ [24]. This compound did not disappear during the Z-W test of Samples 1 and 2, but it was rapidly degraded during the photo-Fenton treatment and was no longer observed at $t_{30w} > 50$ min (S3–S6 samples). This product was followed by LC–TOF–MS (ESI+), and additional hydrolysis experiments were carried out to corroborate these results. The decay in pyrimethanil was due to adsorption on the biomass. This was demonstrated by a desorption step of biomass with acetonitrile after the Z-W test, in which the amount of pyrimethanil detected was in agreement with the original mass balance. Therefore, as expected, these five compounds are nonbiodegradable. As shown in Fig. 6, Samples 1 and 2 were hardly biodegradable, with only 50 and 60% biodegradability after nine days of biotreatment respectively. As biodegradation of wastewater is usually easier in large-scale bioreactors than in Z-W tests, Sample 2 might reach the biodegradability threshold in a biological reactor. However, as the pesticides (active ingredients in the commercial formulation) have proved to be recalcitrant, they would hardly be degraded at all by the biotreatment. To properly interpret Sample 2 results, it should be mentioned that Z-W takes the overall DOC into

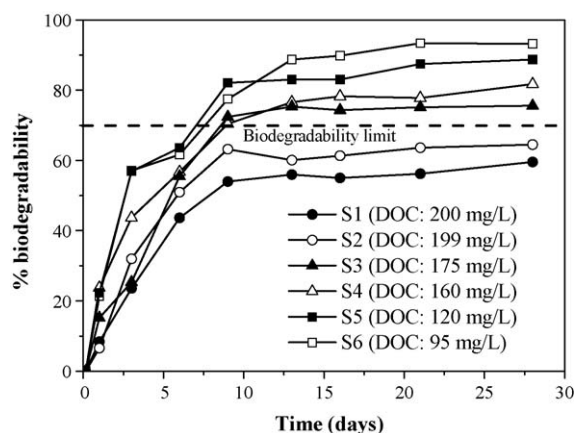


Fig. 6. Zahn–Wellens (Z-W) biodegradability analysis of photo-Fenton samples (as labeled in Fig. 5).

consideration and only 17% of the DOC in the commercial pesticide formulation was from active ingredients. On the other hand, all samples without pesticides reached at least 70% of biodegradability in nine days ($\text{DOC} < 175 \text{ mg/L}$, see Fig. 6).

The continuous enhancement of biodegradability fits well with the continuous increase in AOS and reduction in toxicity. Feasible combination of photo-Fenton and a biological treatment was demonstrated for the detoxification of the commercial pesticide mixture. To optimize the combined system and reduce costs, the photo-Fenton process should be as short as possible, so as much DOC as possible must be eliminated by the biotreatment, which has been demonstrated to be more cost efficient and environmentally friendly [25]. Then as shown by the results above, the photocatalytic stage should end when elimination of the active ingredients is complete. Recalling the photo-Fenton experiments with different iron species and at different concentrations, the H_2O_2 required only for degrading the active ingredients is significantly lower (between 15 and 17 mM) than consumption required for 75% mineralization with both 20 and 55 mg/L and both iron species (see Table 1). However, the illumination times required for this are slightly lower with 55 mg/L, because there is more catalyst present. Furthermore, H_2O_2 consumption is one of the most relevant photo-Fenton optimization parameters, and working at 20 mg/L of iron avoids the need for iron removal before harmlessly discharging into an aerobic biological treatment. This corroborates the selection of 20 mg/L as the most suitable iron concentration for photo-Fenton as a biological system pretreatment only until total elimination of the active ingredients.

4. Conclusions

In this study, solar photo-Fenton was employed as a pretreatment to enhance the biodegradability of a mixture of five commercial pesticides. The conclusions drawn from this work are summarized as follows:

- (1) The use of ferrous or ferric ions as the catalyst source in Fenton reactions is not critical, as results were comparable for both in terms of degradation of active ingredients and mineralization. Ferrous ions were slightly more active than ferric which can be attributed to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox cycle inducing fast formation of reactive radicals.
- (2) On the other hand, the improvement with solar irradiation over the dark reaction was clearly demonstrated. Under identical conditions, Fenton treatment would have to be 40 times longer than photo-Fenton to achieve complete pesticide elimination and even longer for comparable mineralization. 20 mg/L was considered the most suitable iron concentration in tubular solar photoreactors with a diameter of a few cm.

- (3) The minimum requirement for successfully switching from chemical pre-oxidation to biological post-treatment would be the elimination of active pesticide ingredients, as demonstrated by ecotoxicity and aerobic biodegradability assays.

Acknowledgments

The authors wish to thank the Spanish Ministry of Education and Science for its financial assistance under the “Fotobiox” Project (Ref. CTQ2006-14743-C03-01). The valuable collaboration of the Almería wastewater treatment plant (AQUALIA) is much appreciated. Ana Zapata would like to thank the Spanish Ministry of Education and Science for her Ph.D. research grant. T. Velegriaki would like to thank the TUC Research Committee for sponsoring her stay at the Plataforma Solar de Almería.

References

- [1] EU Directive 2000/60/EC of the Council and the European Parliament of 23 October 2000, OJL 237, 2000.
- [2] P.R. Gogate, A.B. Pandit, *Adv. Environ. Res.* 8 (2004) 501.
- [3] M. Bressan, L. Liberatore, N. D'Alessandro, L. Tonucci, C. Belli, G. Ranalli, *J. Agric. Food Chem.* 52 (2004) 1228.
- [4] J.M. Herrmann, *Top. Catal.* 14 (2005) 48.
- [5] G. Sagawe, A. Lehnard, M. Lübber, D. Bahnemann, *Helv. Chem. Acta* 84 (2001) 3742.
- [6] C. Comninellis, A. Kapalka, S. Malato, S.A. Parsons, I. Polios, D. Mantzavinos, *J. Chem. Tech. Biotechnol.* 83 (2008) 769.
- [7] C. Pulgarín, M. Invernizzi, S. Parra, V. Sarria, R. Polaina, P. Péringier, *Catal. Today* 54 (1999) 341.
- [8] V. Sarria, S. Parra, N. Alder, P. Péringier, N. Benítez, C. Pulgarín, *Catal. Today* 76 (2002) 301.
- [9] R.F.P. Nogueira, C.O. Mirela, W.C. Paterlini, *Talanta* 66 (2005) 86.
- [10] United States Environmental Protection Agency, Prevention, Pesticides and Toxic Substances (7101), Fates, Transport and Transformation Test Guidelines OPPTS 835.3200 Zahn–Wellens/EMPA Test, EPA 712-C-96-084, 1996.
- [11] M. Lapertot, C. Pulgarín, P. Fernández-Ibáñez, M.I. Maldonado, L. Pérez-Estrada, I. Oller, W. Gernjak, S. Malato, *Water Res.* 40 (2006) 1086.
- [12] S. Malato, J. Blanco, A. Vidal, D. Alarcón, M.I. Maldonado, J. Cáceres, W. Gernjak, *Sol. Energy* 75 (2003) 329.
- [13] J. Blanco-Galvez, P. Fernández-Ibáñez, S. Malato-Rodríguez, *J. Solar Energy Eng.* 129 (2007) 4.
- [14] R. Bauer, G. Waldner, H. Fallmann, S. Hager, M. Klare, T. Krutzler, S. Malato, P. Maletzky, *Catal. Today* 53 (1999) 131.
- [15] R.G. Zepp, B.C. Faust, J. Hoigné, *Environ. Sci. Technol.* 26 (1992) 313.
- [16] J.J. Pignatello, E. Oliveros, A. MacKay, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1.
- [17] H. Gallard, J. De Laat, *Water Res.* 34 (2000) 3107.
- [18] C. Segura, C. Zaror, H.D. Mansilla, M.A. Mondaca, *J. Hazard. Mater.* 150 (2008) 679.
- [19] I. Oller, S. Malato, J.A. Sánchez-Pérez, M.I. Maldonado, R. Gassó, J. Blanco, *Catalysis Today* 129 (2007) 69.
- [20] C. Walling, *Acc. Chem. Res.* 8 (1975) 125.
- [21] W. Gernjak, M. Fuerhacker, P. Fernández-Ibáñez, J. Blanco, S. Malato, *Appl. Catal. B: Environ.* 64 (2006) 121.
- [22] S. Parra, V. Sarria, S. Malato, P. Péringier, C. Pulgarín, *Appl. Catal. B: Environ.* 27 (2000) 153.
- [23] J.P. Scott, D.F. Ollis, *J. Adv. Oxid. Technol.* 2 (1997) 374.
- [24] J. Harvey Jr., J.C.-Y. Han, *J. Agric. Food. Chem.* 26 (1978) 536.
- [25] I. Muñoz, J. Peral, J.A. Ayllón, S. Malato, M.J. Martín, J.Y. Perrot, M. Vincent, X. Domènech, *Environ. Eng. Sci.* 24 (2007) 638.